Chapter 1
General Introduction

Abstract The polymeric metal chelates present class of chemical compounds including polymeric chain (organic, inorganic, mixed or biological nature) and metal chelate cycles. This direction of chemical science has appeared in the last decades of twentieth century at the junction of different fields of knowledge: coordination, polymer, physical, organic, colloid chemistry, biology, medicine and materials science. The need for accelerated development of this direction is confirmed by a rapid increase in the number of publications devoted to the study of polymeric metal chelates and their use as precursors of functional and nanoscale materials. Despite the variety of existing methods for synthesizing polymeric metal chelates, the main method still remains the direct interaction of metal compounds with chelating polymeric ligands. Therefore, the molecular design of chelating macroligands is an important, and in some cases, defining task both from the point of view of obtaining metal chelates with predetermined properties and structure, and their subsequent practical use. At the same time, in recent years a number of new methods have been developed for the preparation of polymeric metal chelates, primarily on the basis of metal chelate monomers, which allow one to obtain complexes in one stage with a targeted composition and structure. Progress in this field of chemistry is also associated with the emergence of new types of polymeric metal chelates, in particular, metal chelate dendrimers, star and hyperbranched polymers, as well as coordination polymers and supramolecular metal chelate polymers.

Characteristic features, allowing reliably identify the polymeric metal chelates (PMCs) as particular class of chemical compounds, is the presence of the polymeric chain (organic, inorganic, mixed or biological nature) and metal chelate cycles [1]. This area is interesting because it is located at the intersection of the boundary areas of science—polymer and coordination chemistry. The combination of metal chelates and polymers in one chemical entity represents, on one hand, a fairly complex way, where in each case we have to use their methods of synthesis and study. PMCs are highly interesting materials with properties combining typical polymeric features with the properties of metal chelates. Due to the polymer chain, PMCs behave

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in many cases like ordinary macromolecular compounds, and due to the presence of metal ion in the chain, PMCs exhibit properties characteristic of a given metal ion. On the other hand, it is at the junction of polymer and coordination chemistry can expect the unexpected multidimensional spatial architectures of the polymer chains and new regularities in the formation of supramolecular structures, and hence the unusual properties of the resulting materials (catalytic, magnetic, electrical, nonlinear-optical, etc.).

These advanced metal chelate—polymeric structures can be considered from two different points of view: the only scientific knowledge or practical orientation [1–21]. In particular, PMCs allowed making significant progress in solving many theoretical problems of modern chemistry. These include the architecture of polymers, the reactivity of macromolecules, the specificity of metal chelation by polymer ligands, the synthesis of polynuclear metal chelates, competing coordination, the preparation of immobilized catalysts, and so on. Of no small importance is the fact that PMCs have multiple potential applications including catalysis, polymer light-emitting diodes (PLED), nonlinear optical (NLO) devices, sensors etc. [22–37]. In addition, it should be noted their biomedical and pharmaceutical applications as drug delivery carriers, metal-containing drugs, photodynamic therapy (PDT) agents, biosensors, and bioimaging agents [3, 5, 38–43]. PMC are ideal for building dynamic molecular systems whose movements are controlled from the outside [44, 45]. As a rule, these compounds are called «molecular machines». Self-assembly of PMC allows you to create unique spatial architectures, so they can, for example, serve as a precursor to the fabrication of the «technomimetic spoked wheels» [46, 47]. Another example of self-assembly of PMC is synthetic, in nanometer scale, «Sierpinski hexagonal gasket» [48, 49]. This nondendritic, perfectly self-similar fractal macromolecule consists of bis-terpyridine building units, which are interconnected coordination of 36 Ru and 6 Fe ions, forming a nearly flat array of ever-larger hexagons around an empty center. Finally, the self-assembling PMC on the various nanostructures and surfaces [50–53] is considered in this context.

By formal features, methods of producing PMC, representing polymer matrix in which the metal chelate units are distributed, do not differ from the most common approaches to the synthesis of metal chelates without polymer. Therefore, modern synthetic PMC chemistry is based on the general methods and principles of the synthesis of coordination compound. As in the case of low molecular weight metal chelates (LMCs), most currently known PMCs are obtained by the direct interaction of metal compounds (MX_n) with chelating polymer ligands (CPLs). Therefore, the design of CPL is an important, and in some cases, and decisive problem in terms of obtaining PMC and their future practical use. CPLs are macromolecular compounds (organic, inorganic, mixed or biological nature) with polydentate functional groups capable of forming a metallocycle by reacting MX_n. Currently there is no uniform classification of CPL. Apparently, such classification should consider the following: nature and preparation method of CPL (organic, inorganic, mixed or biopolymers); method and step number of functionalization (polymerization, polycondensation and post-polymerization modification); physical characteristics of the polymer (homopolymers, copolymers, branched, cross-linking, grafted polymers, dendrimers, hyperbranched polymers, liquid crystalline polymers, polymeric films, etc.); structural organization of the polymer (molecular, supramolecular and topological levels); characteristic of the chelating fragments (structure, type, concentration, nature of the donor atoms, etc.).

Synthetic polymeric organic compounds containing chelating fragments represent the largest group of CPL. Their characteristic features are:

- the large number of functional (chelating) groups and comparative ease of their modification;
- a wide range of specific surface areas and pore sizes;
- controlled swelling and solubility in the reaction medium;
- adjustable mobility of chain segments (and, accordingly, chelating fragments);
- low adsorbability and stability over a wide pH range;
- weak physical adsorption capacity;
- possibility of introduction of chelating groups at the stageof the preparation and forecasting their distribution.

It should be noted that by formal features any interaction in the MX_n—CPL system can be considered as chelation reaction (multipoint metal binding with one polymer). Thus, the polydentate immobilization of a metal is often observed in the case of the polymers with monofunctional groups, for example, polyvinylpyridines, polyacids, polyvinyl alcohol, etc. And both mono- and bidentate intra- and intermolecular metal binding are observed in these systems. However, polymer ligands with monofunctional groups will not be considered in the book.

On the other hand, in recent year propagation are PMCs, in which the metal chelate units are located only on the surface of the powder, films, fibers, and PMCs may have not only three, but even two or one dimension.

Unfortunately, long time the metal chelates based on synthetic polymers belong to PMCs. However, according to the definition the metal chelates with inorganic, mixed and biopolymeric ligands are PMCs, because, for example, mostbiopolymers (DNA, RNA, enzymes, etc.) are the metal chelate macromolecular compounds. It defines the importance of PMCs in the vital functions of organisms, because the metals, for example, take place in binding of nucleic acids to proteins. The latter has a significant influence in their resistance to denaturation, the proceeding protein synthesis and the preservation of genetic information. In this connection, extensive studies were conducted to investigation of the metal chelation with biopolymer ligands and creation of their synthetic analogues. It should be noted that there are about 30 different metals used in polymeric systems for biomedical applications (Fig. 1.1) [43].

It should be noted the study of the metal chelates based on inorganic and mixed carriers, which develops in two directions: the modification of mineral carriers in order to the creation of chelating fragments on their surface followed the preparation of the metal chelates, and synthesis of the chelating macroligands based on mixed carriers.

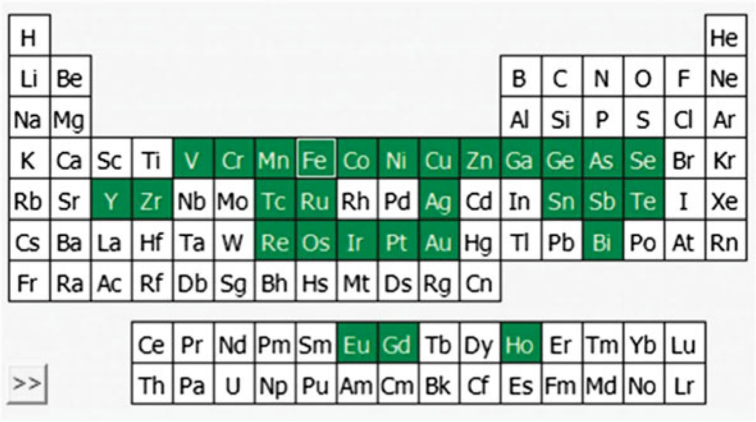

Fig. 1.1 Metals in periodic table used in polymeric systems for biomedical applications

The quantitative parameters of chelation process with the participation of the polymer ligands so far not been adequately studied in contrast to LMCs. This is due to the need to take into account a number of additional factors, mainly related to the chain nature of the polymer ligand. It is expedient to consider three levels of the spatial organization of PMCs [54]:

1. local level, which reflects the chemical and spatial structure of a single metal chelate cycle in the polymer chain (nature of the donor atoms and a center metal, cycle size, its electronic and spatial structure, etc.);
2. molecular level, defined by the spatial and chemical structure of the polymer chain (the elemental composition of monomer units, length, shape and conformation of a polymeric chain, etc.);
3. supramolecular level, reflecting the character of the intermolecular interaction of the polymer chains and the degree of their mutual ordering.

Taking these three levels of the spatial organization of the PMC into account, the free energy of the chelation involving macroligands can be represented (on the assumption that its components are additive) by the equation:

$$\Delta G = \Delta G_1 + \Delta G_2 + \Delta G_3. \tag{1.1}$$

Here ΔG_1, ΔG_2, and ΔG_3 are the free energy changes for the local, molecular, and supramolecular levels respectively. Under certain conditions, the free energy change for a particular level may be neglected, which makes it possible to analyze in detail the enthalpy (ΔH) and entropy ($T\Delta S$) contributions to ΔG for each level.

$$\Delta G = \Delta H - T\Delta S \tag{1.2}$$

In dilute solutions, chain association may be neglected; therefore $\Delta G_3 \to 0$ and (1.1) can be expressed in the form

$$\Delta G = \Delta G_1 + \Delta G_2. \tag{1.3}$$

In the case of infinitely long chains ($l \to \infty$) and low degrees of conversion[1] with respect to the chain molecule ($\alpha \to 0$), the chelation process may not exert a significant influence on the form and conformation of the macromolecule, so that $\Delta G_2 \to 0$ and hence

$$\Delta G = \Delta G_1 \tag{1.4}$$

Thus, in the case of dilute solutions with $l \to \infty$ and $\alpha \to 0$ the CPL behaves similarly to its low molecular weight analogue and the familiar Flory principle then operates: when the components of the model reaction are chosen correctly, the reactivity of the binding sites is independent of whether they belong to the polymer chain or to the low molecular weight analogue. This makes it possible to exclude from consideration the molecular and supramolecular levels and to analyze only the local chelate units.

For example, the entropy and enthalpy components of ΔG in the case of PMCs are determined mainly by the same contributions as in the case of LMCs [55–57]. Since the nature of the complex-forming metal and the chelating fragments is the same in both cases, the enthalpy of chelation changes little on passing from LMC to PMC. Therefore, for both LMC and PMC ΔG is determined by the entropy components. Formally the chelation reaction can be divided into several hypothetical elementary stages and the entropy of the entire process can be expressed as follows:

$$\Delta S_1^0 = \Delta S_{solv} + \Delta S_4^0 = \Delta S_2^0 + \Delta S_3^0 + \Delta S_5^0 + \Delta S_4^0, \tag{1.5}$$

where ΔS_1^0 is the experimental entropy of the reaction in solution, ΔS_4^0 is the calculated theoretical entropy of the reaction in the gas phase, ΔS_{solv} is the entropy of solvation of the metal ion (ΔS_2^0), of the ligand (ΔS_3^0), and of the complex formed (ΔS_5^0), which is determined as the difference between the entropies in solution and in the gas phase.

ΔS_4^0 represents in its turn the sum of the entropies of transfer (ΔS_t), internal rotation ($\Delta S_{int.rot}$), symmetry (ΔS_{sym}), isomerization (ΔS_{isom}), vibration (ΔS_{vib}), and rotation (ΔS_{rot}).

$$\Delta S_1^0 = \Delta S_{solv} + \Delta S_t + \Delta S_{int.rot} + \Delta S_{sym} + \Delta S_{isom} + \Delta S_{vib} + \Delta S_{rot} \tag{1.6}$$

It is assumed that the positive contributions to the entropy component of ΔG come from ΔS_t, ΔS_{rot}, ΔS_{sym}, and ΔS_{isom}. The contribution of ΔS_t, due to the

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[1] The degree of conversion α is defined as the ratio of the actual number of metal ions bound to one chain and the maximum possible number.

change in the number of species on chelation, apparently changes little on passing from LMC to PMC. Consequently, the entropies of chelation are similar in the two cases, since the contribution of the transfer process is the main one. ΔS_{rot} makes a definite contribution to the entropy component. It is smaller in the case of PMC than in the reaction with monodentate ligands because the initial CPL and the PMC formed are the nonrotating species. The symmetry groups for low and high molecular weight compounds are significantly different and the number of possible isomers of PMC may be smaller, so that the contribution of isomerization is in this case reduced.

ΔS_{vib}, $\Delta S_{int.rot}$, and ΔS_{solv} make negative contributions to the entropy component. It is postulated that the contributions by the vibration and internal rotation are much lower in the case of the PMC than in the case of the LMC. If the monomeric and polymeric chelating ligands form structurally identical chelate fragments, then the contribution of solvation is approximately the same in both cases. However, as a rule such cases are rare and the polymer chain exerts a significant influence on the structure of the local chelate unit with the possibility of the formation of structures which are both less and more distorted than in the LMC.

The classification of PMCs adopted in this monograph includes four types of compounds: molecular, intracomplex, macrocyclic and polynuclear metal chelates. In the PMCs of molecular type, the metal ion chelation proceeds only through coordination bonds. Binding a metal ion by both the covalent and coordination bonds is characteristic for the PMCs of intracomplex type. Metal chelation of the CPLs contained macrocyclic groupings leads to the PMCs of macrocyclic type. Finally, polynuclear metal chelates contain two or more metal ions, and at least one of them must be part of the metallocycle. In following, PMCs are classified depending on the nature of the donor atoms (N,N–, N,O–, N,S–, O,O–, etc.).

Synthetic methodologies of PMCs in most cases consist of a series of sequential operations involving the preparation of a polymeric carrier, its functionalization towards the creation of chelating fragments, binding of MX_n, and purification of the final product. Sometimes, it is possible to achieve a reduction in the number of synthetic steps, which makes it possible to significantly simplify the entire technological chain, increase the overall yield and reduce the cost of the target product. One of the promising avenues for solving this complex problem is the one-stage synthesis of PMC, based on the (co)polymerization or polycondensation of metal chelate monomers (MCM) [1, 3, 10, 11, 14, 16, 18, 24, 30, 58–65]. Such compounds include a metal chelate ring and double bonds for (co)polymerization or functional groups for polycondensation. The undoubted advantage of this method is the possibility of purposeful production of PMCs, in which a metal ion with a predetermined spatial configuration of the chelate unit is contained in each chelating fragment.

The creation of dendrimers becomes an important landmark in the development of contemporary coordination chemistry. One of important classes of PMC is metal chelate dendrimers (MCDs) containing chelated metals in different parts of dendritic architecture, which have been obtained in the first days of dendrimer chemistry and are objects of increasing interest of researchers [66–69]. Metal chelate dendrimers are relatively young, but rapidly developed area of PMC chemistry. Simultaneously with the metal chelate dendrimers the first examples of star and hyperbranched materials containing metal chelate units were prepared.

Extended hybrid crystalline complex compounds formed by organic ligands (also called spacers) and metal ions expanding in one, two or three dimensions due to formation of metal-ligand (M-L) coordination bond are called coordination polymers (CPs) [70–77]. CPs relate to a special class of PMCs containing metal in the main chain, whose special feature is breaking of a polymer chain after a metal is removed. First time the term «coordination polymer» was used in 1964 [78]. At the first stage of the studies, CPs were obtained using a simple mixing of components or the template method, as a result, insoluble substances were formed, whose exact structure was non-improvable. A great jump in directed design of CPs was done in 1990s by wide implementation of new techniques of synthesis of such materials, first of all, solvothermal method [79, 80], which made it possible to obtain pure substances useful for research by X-ray diffraction analysis. By controlling the process of CP molecular self-assembling, it is possible to obtain new crystalline functional materials with given practical properties. Because they contain large voids in the crystal structure, they were called porous CPs or metal-organic frameworks (MOFs). This term MOF was popularized around 1995 [81, 82] and it highlights their similarity to traditional structure of solids, in particular, zeolite framework materials, and thus characterizes reliability and porosity. MOFs differ by interesting architecture, crystalline state, capable of modifying the surface, and have potential applications in the areas of gaseous fuel storage, catalysis, magnetism and separation. Integration of MOFs become a real outbreak in science and served a powerful catalyst of intense development of CP chemistry.

Today it is absolutely clear that within relatively short time interval, with respect to historical scale, supramolecular chemistry has turned into very rapidly developed and interdisciplinary science, which includes chemical, physical, and biological aspects of studying more complicated than molecules chemical systems assembled into integral whole through intermolecular (non-covalent) interactions [83–89]. The supramolecular systems have a special niche, a level in hierarchy of matter, in which such principles of organizing and functioning of matter as molecular recognition, selective bonding, receptor-substrate interaction, trans-membrane transfer, and supramolecular catalysis are realized. Among the supramolecular systems the metallosupramolecular polymers (MSPs), which include metal-containing fragments as a basic supramolecular motif and formed as a result of spontaneous self-assembling of polytopic organic ligands and metal ions, represent of special interest [90, 91]. Concept of metallosupramolecular polymerization requires that a chelating monomer would be a telechelic system capable of continuous elongation of a chain in presence of a metal ion via well-known consecutive polycondensation mechanism. MSPs can be considered as a subset of PMCs, in which M-L interaction is dynamic by its character. These organic/inorganic hybrid systems potentially offer attractive combination of functionality of metal ions, mechanical properties and workability of polymers, as well as characteristics of self-assembling and dynamic character of supramolecular chemistry.

Among the most interesting areas of practical application of PMCs is the preparation of nanomaterials with low crystalline defects, narrow size distribution, and tunable shapes by their high-temperature thermolysis [92, 93]. From the view of the design of functional nanomaterials, solid-state thermolysis of PMCs possessing the wide diversity of the structures, compositions, and architectures is a simple and rational route to synthesize novel nanostructured materials. It should be noted the development of many important concepts such as size distribution focusing, selective adhesion shape control and branching for the description of the thermolysis process [93–96]. Thermolysis of PMC under various conditions is widely studied to obtain metal-containing nanostructures with target morphologies and sizes [2, 3, 6, 14, 15, 19, 20, 97–104]. It is important that different nanomaterials such as metals, metal oxides, metal sulfides and metal halides can be fabricated using PMC or their precursors.

The history of PMC research originates from the period of the Second World War and was stimulated, in the main, by tasks of a practical nature [1]. However, over the years, the development of PMC chemistry has been hampered by the lack of readily available synthesis techniques, difficulties in purifying the end products and convincing methods of their identification. In the early 1990s, a significant breakthrough was made in the synthesis of PMCs, which allowed the production of macromolecular soluble materials with well-defined spatial architectures. As a typical example, we note numerous synthetic methodologies of PMCs involving Schiff bases (Fig. 1.2).

These achievements allowed, in a figurative expression [105], to open a Pandora box of metal-containing polymers with new technological properties [106–114]. It

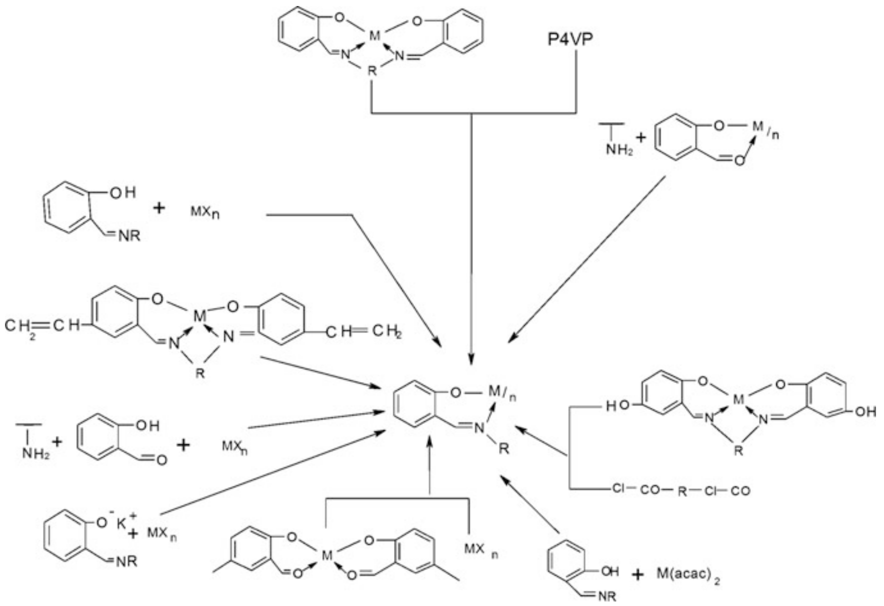

Fig. 1.2 Main directions of the synthesis of PMCs including Schiff bases

should also be noted the use of PMCs to obtain stimuli-responsive, self-healing, and shape-memory materials due to reversible metal-ligand interactions [115–119]. Extensive research of such materials began only in the last decade. Also of interest are such interesting objects as self-organizing and hierarchical architectures based on PMCs.

It should be noted the development of PMC studies as precursors of nanostructured materials, including carbon, metals, metal oxides, mixed metal oxides, etc. It is important that PMCs act not only as raw materials, but also as stabilizers of the formed nanoparticles, forming a protective shell [2, 6, 14, 15, 19, 20, 120, 121]. In recent decades, the use of PMC in nanotechnology and organic electronics, in particular in organic solar cells, nanowires, sensors, light-emitting devices, etc., has attracted considerable attention.

This book covers the major advances in the synthetic methodologies, physicochemical properties, and spatial organization of polymeric metal chelates, and includes chapters on the synthesis and characterization of chelating polymer ligands, metal chelates based on synthetic polymers, metal chelate monomers, metal chelate dendrimers, coordination polymers containing metal chelate units, metal chelate supramolecular polymers, as well as thermolysis of metal chelate polymers. We hope that the analysis of the achievements and problems of the chemistry of polymeric metal chelates will contribute to a more accelerated development of this interesting and fascinating field of chemistry.

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